Organic Process Research & Development **2003**, *7*, 161–163

Direct Sulfonation of Methane at Low Pressure to Methanesulfonic Acid in the Presence of Potassium Peroxydiphosphate as the Initiator

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Abstract:

A high-yield, direct sulfonation of methane with SO_3 to methanesulfonic acid (MSA) is effected in sulfuric acid using potassium peroxydiphosphate ($K_4P_2O_8$) as the initiator. The influences of initiator concentration, temperature, CH_4 pressure, the initial concentration of SO_3, and solvent acidity were investigated. A mechanism is proposed to explain the observed effects of reaction conditions on the conversion of SO_3 to MSA.

Introduction

The selective catalytic functionalization of methane to value-added products is a subject of considerable contemporary interest.[1] Because of favorable thermodynamics, many researchers have investigated the oxidation and oxidative carbonylation of methane.[2]By contrast, the sulfonation of methane has not yet received as much attention despite of its commercial importance.[3] The current commercial process for the synthesis of methanesulfonic acid (MSA) involves the chlorine oxidation of methylmercaptan.[4] While this process is highly productive, it produces six moles of HCl per mole of MSA, resulting in a coupling of the demand for the primary product and the byproduct. Thus, there is an incentive to find a method for the direct methane sulfonation of methane, which avoids the coproduction of HCl. Sen and co-workers[5] and, more recently, we[6,7] have shown that $K_2S_2O_8$ can be used as a free radical initiator to sulfonate methane with SO_3 in fuming sulfuric acid under 1000 psig methane pressure. In the latter work, it was shown that, with increasing reaction temperature, the conversion of SO_3 to MSA, the limiting reagent, reaches a maximum at 65 °C. Above this temperature, O_2 released due to initiator decomposition inhibits the free-radical processes involved in the formation of MSA. In view of this, the question arises as to whether one might be able to use potassium peroxydiphosphate ($K_4P_2O_8$) as the initiator, since this material is more stable to decomposition and release of O_2 than $K_2S_2O_8$.[8] In this work, we show that methane will undergo liquid-phase sulfonation to MSA with SO_3 in sulfuric acid, using a small amount of $K_4P_2O_8$ as a free radical initiator and that this initiator is more effective than $K_2S_2O_8$ at elevated temperature.

Table 1. **Direct free radical initiated sulfonation of methane with SO_3[a]**

initiator	time, h	% conversion of SO_3 to MSA
$K_4P_2O_8$	12	21
$K_2S_2O_8$	14	11
Oxone[b]	14	3
H_2O_2	16	5

[a] Reaction conditions unless otherwise stated: methane, 200 psig (58 mmol); SO_3, 30 wt % (21.4 mmol); initiator, 0.104 mmol; temperature, 95 °C; H_2SO_4 (SO_3), 5.7 g. [b] Potassium peroxymonosulfate

Results and Discussion

In a typical reaction (see Experimental Section) methane was reacted with SO_3 in H_2SO_4 to form MSA in the presence of $K_4P_2O_8$ in a high-pressure, glass-lined Parr autoclave. Reactions were carried out for 12 h, and the MSA thus formed was identified and quantified by ^{1}H NMR.[6,7]

Table 1 shows the effect of different promoters on the rate conversion of SO_3, the limiting reagent, to MSA. Using $K_4P_2O_8$ as the initiator, a 21% conversion of SO_3 to MSA was achieved in 12 h. Under identical reaction conditions, the conversion of SO_3 to MSA decreased to 11% when $K_2S_2O_8$ was used as the initiator. When Oxone ($KHSO_5$) was used as the initiator, only a 3% conversion of SO_3 to MSA was achieved in 14 h. Similarly, a conversion of 5% was obtained using 30 wt % H_2O_2 as the initiator. In this last case, additional SO_3 was added to the reaction mixture to convert the water in the peroxide solution to H_2SO_4.

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10.1021/op020079n CCC: $25.00
Published on Web 01/30/2003

Table 2. **Direct free radical initiated methane sulfonation with SO_3[a]**

entry	parameters	time /h	% conv. of SO_3 to MSA
1	$K_4P_2O_8$, 0 mmol	12	0
2	0.052 mmol	12	14
3	0.104 mmol	12	21
4	0.104 mmol	6	12
5	0.208 mmol	12	16
6	Temperature, 85 °C	12	7
7	95 °C	12	21
8	105 °C	12	14
9	CH_4, 50 psig	14	2
10	80 psig	12	6
11	120 psig	12	9
12	200 psig	12	21
13	SO_3, 15 wt %	12	11
14	30 wt %	12	21
15	38 wt %	12	26
16	52 wt %	12	19

[a] Reaction conditions unless otherwise stated: methane, 200 psig (58 mmol); SO_3, 30 wt % (21.4 mmol); initiator, 0.104 mmol; temperature, 95 °C; H_2SO_4 (SO_3), 5.7 g.

Table 2 shows the effects of reaction conditions on the conversion of SO_3 to MSA, using $K_4P_2O_8$ as the initiator. Entries 1−5 show that the conversion of SO_3 to MSA increases with the amount of $K_4P_2O_8$ added to the reaction mixture up to a value of 21%. Addition of more than 0.104 mmol of $K_4P_2O_8$ reduced the conversion of SO_3 to MSA. In contrast to $K_2S_2O_8$, which is most effective in the temperature range of 65−70 °C, $K_4P_2O_8$ is most effective at 95 °C (Table 2, entries 6−8). At higher temperatures, the conversion of SO_3 to MSA decreases with increasing temperature. It should be noted, though, that when the effectiveness of $K_2S_2O_8$ and $K_4P_2O_8$ is compared at 65 °C with all other reactions conditions as shown for entries 6−8, then the conversion of SO_3 to MSA is 4% using $K_2S_2O_8$ as the initiator and 2% using $K_4P_2O_8$ as the initiator. Entries 9−12 show that the conversion of SO_3 to MSA increases monotonically from 2 to 21% as the pressure of CH_4 is increased from 50 to 200 psig. The conversion of SO_3 to MSA is also a fucntion of the initial SO_3 concentration (Table 2, entries 13−16). With an increase in concentration from 15 to 38 wt %, the SO_3 conversion to MSA increased from 11 to 26%. However, increasing the intial SO_3 concentration up to 52% caused a decrease in the conversion of SO_3 to MSA.

Previous studies in which $K_2S_2O_8$ was used as the initiator have shown that for a given set of reaction conditions, the conversion of SO_3 to MSA increases with the acidity of the solvent. This effect was attributed to an increase in the rate of initiator decomposition to produce radical anions, $SO_4^{-\bullet}$.[7] As discussed below, radical anions are believed to be responsible for initiating a sequence of elementary processes that lead ultimately to MSA. A similar influence of solvent acidity was observed using $K_4P_2O_8$ as the initiator. As supplied by Aldrich, $K_4P_2O_8$ contains 5 wt % KF. This compound reacts with H_2SO_4 to produce HF in situ. To achieve a higher acidity, the HF was reacted with SbF_5 (0.008 mmol) to form magic acid, $HSbF_6$.[9] For all other reaction conditions being the same as those for entry 7 in Table 2, the conversion of SO_3 to MSA increased from 21% without SbF_5 to 30% upon SbF_5 addition.

Scheme 1. **Proposed reaction mechanism**

$$P_2O_8^{4-} \rightleftharpoons 2PO_4^{2-}\cdot \quad (1)$$

$$CH_4 + PO_4^{2-}\cdot \longrightarrow CH_3^{\bullet} + HPO_4^{2-} \quad (2)$$

$$CH_3^{\bullet} + SO_3 \longrightarrow CH_3SO_3^{\bullet} \quad (3)$$

$$CH_3SO_3^{\bullet} + CH_4 \longrightarrow CH_3SO_3H + CH_3^{\bullet} \quad (4)$$

The experimental results reported here can be interpreted by a mechanism that is analogous to that previously proposed for the $K_2S_2O_8$-initiated sulfonation of methane.[6,7] As shown in Scheme 1, reaction begins with the decomposition of the initiator breaks in to two radical anions (reaction 1). The radical anions thus formed then abstract a hydrogen atom from methane and generate a methyl radical (reaction 2). The methyl radical in turn reacts with sulfur trioxide to generate methanesulfonyl radicals (reaction 3), which subsequently abstract hydrogen from another methane molecule to form the product, MSA (reaction 4). In support of the proposed mechanism, we note that at the end of the reaction, ^{31}P NMR reveals that all of the initiator has been converted to K_2HPO_4, consistent with what would be expected from reaction 1.

The observed lowering in the conversion of SO_3 to MSA when more than 0.104 mmol of initiator is used can be attributed to the high rate of formation of free O_2 by the thermal dissociation of $K_4P_2O_8$. Oxygen released in this manner can act as a free-radical scavenger, thereby inhibiting the formation of MSA.[5] This interpretation is consistent with the failure to observe any MSA when the reaction was carried out in the presence of 30 psig of O_2. The decrease in SO_3 conversion for temperatures above 95 °C is attributed to an increasing release of O_2, which offsets the favorable effect of increasing temperature on the reaction kinetics.

Since SO_3 is an essential component of MSA, the rise in SO_3 conversion to MSA with increased initial concentration of SO_3 is not surprising. The decrease in SO_3 conversion to MSA once the initial SO_3 concentration rises to 52 wt % is possibly due to the removal of dissolved SO_3 through the formation of products such as $H_2S_2O_7$, $H_2S_3O_{10}$, $H_2S_4O_{13}$, and so forth.[10] The other contributors to the decrease in the conversion of SO_3 to MSA is the formation of methanedisulfonic acid (0.5−1%), and $CH_3(SO_3)_2H$ (0.3−0.4%), which are observed at SO_3 concentrations above 38 wt %.[7]

Conclusions

We have demonstrated that the direct sulfonation of methane to MSA can be achieved using $K_4P_2O_8$ as the initiator. The highest conversion of SO_3 to MSA is achieved at 95 °C. Comparison of the relative performance of $K_2S_2O_8$ and $K_4P_2O_8$ reveals that while the former initiator is more active, the latter can be used at higher temperatures because

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of its higher thermal stability to decomposition and release of O_2, a reaction inhibitor. The net result is that a higher conversion of SO_3 to MSA can be attained at 95 °C using $K_4P_2O_8$ as an initiator, all other reaction conditions being equal. The reaction mechanism proposed in Scheme 1 offers an effective basis for explaining the observed effects of reaction conditions.

Experimental Section

Reactions were carried out in a 100-mL high-pressure autoclave (Parr Instruments, 3000 psig maximum) constructed of Hastelloy B. Unless otherwise stated, the following procedure was used for all experiments. $K_4P_2O_8$ (0.104 mmol) (Aldrich, tech.) and 5.7 g of fuming sulfuric acid (Aldrich Chemical Co., 27−33% SO_3) were added to a glass liner containing a Teflon-encased stirring bar. For some experiments, additional SO_3 (Aldrich Chemical Co., 99%) was added to the liquid in the liner. The glass liner was then transferred to the reactor, after which the reactor was sealed and attached to a gas-handling system. The reactor was purged with N_2 (Matheson, ultrahigh purity) and CH_4 (Matheson, ultrahigh purity) and then pressurized to the desired level with 200 psig CH_4. The reactor was heated to 95 °C, a process which took 8−10 min, and this temperature was then maintained for up to 12 h, unless stated otherwise. Following reaction, the reactor was cooled in an ice bath to room temperature (∼0.5 h), the system was then purged with N_2 purified by passage through oxysorb, ascarite, and molecular sieve traps. The gases exiting the reactor were passed through scrubbers containing NaOH and Carbusorb to remove sulfur (II) compounds. The liquid product was removed from the glass liner and added slowly to 0.5 g of H_2O to convert any unreacted SO_3 to H_2SO_4. Reaction products were characterized by ^1H NMR. All spectra were acquired using a Bruker AMX-400 MHz FT-NMR spectrometer. A capillary containing D_2O and CH_3OH, immersed within the NMR tube containing the sample, was used as a lock, reference, and integration standard. The corresponding chemical shifts for MSA was 2.81−3.04 ppm, depending on the concentration of MSA in the mixture.

Acknowledgment

This work was supported by a grant from ATOFINA Chemicals, Inc.

Received for review September 13, 2002.

OP020079N